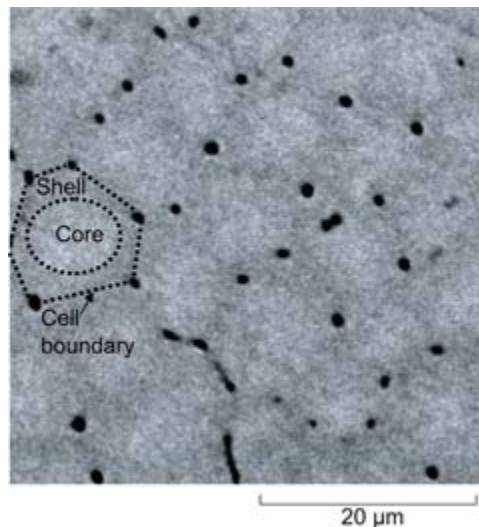


# High-Temperature Proton-Conducting Ceramics Developed

High-temperature protonic conductors (HTPC) are needed for hydrogen separation, hydrogen sensors, fuel cells, and hydrogen production from fossil fuels. The HTPC materials for hydrogen separation at high temperatures are foreseen to be metal oxides with the perovskite structure  $A^{2+}B^{4+}O_3^{2-}$  and with the trivalent cation ( $M^{3+}$ ) substitution at the  $B^{4+}$ -site to introduce oxygen vacancies. The high affinity for hydrogen ions ( $H^+$ ) is advantageous for protonic transport, but it increases the reactivity toward water ( $H_2O$ ) and carbon dioxide ( $CO_2$ ), which can lead to premature membrane failure. In addition, there are considerable technological challenges related to the processing of HTPC materials. The high melting point and multi-cation chemistry of HTPC materials creates difficulties in achieving high-density, single-phase membranes by solid-state sintering. The presence of secondary phases and grain-boundary interfaces are detrimental to the protonic conduction and environmental stability of polycrystalline HTPC materials.

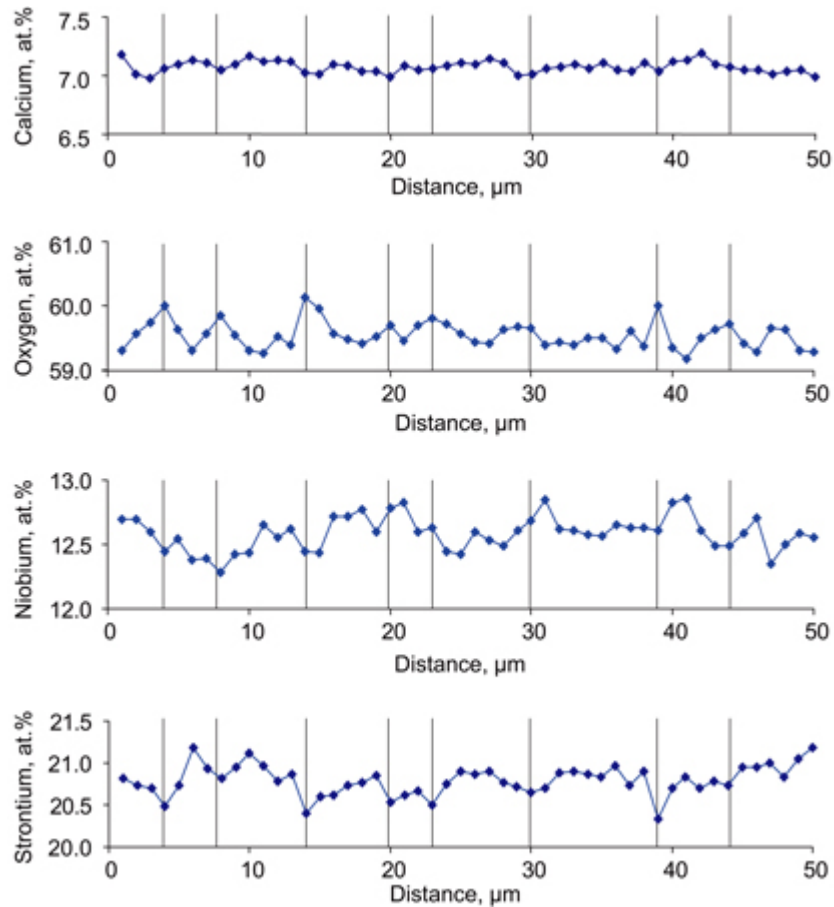
This investigation at the NASA Glenn Research Center explored the prospect of improving the protonic conductance and chemical stability concurrently by producing high-density structures by melt processing. Melt processing of ceramics is being developed to produce engineered microstructures to enhance material properties. The investigation focused on simple  $ABO_3$  and complex  $A_3(B'_{1+x}B''_{2-x})O_{9-\delta}$  perovskite structures using chemical compositions of  $SrCe_{1-x}Y_xO_{3-\delta}$  and  $Sr_3(Ca_{1+x}Nb_{2-x})O_{9-\delta}$ . The advantages of melt processing over solid-state sintering are (1) high-density materials approaching 100 percent are achievable by pore coalescence in the melt; (2) secondary grain boundary phases are eliminated, and coherent low-energy interfaces are formed; and (3) self-assembly produced ordered microstructures at the nanoscale. Melt-processed materials demonstrate stability in high-temperature environments containing high concentrations of water vapor (4 to 6 months).



*Scanning electron microscope photograph of a cross section of  $Sr_3(Ca_{1+x}Nb_{2-x})O_{9-\delta}$*

imaged by back-scattered electrons. Superimposed illustration shows the core, shell, and cellular boundary.

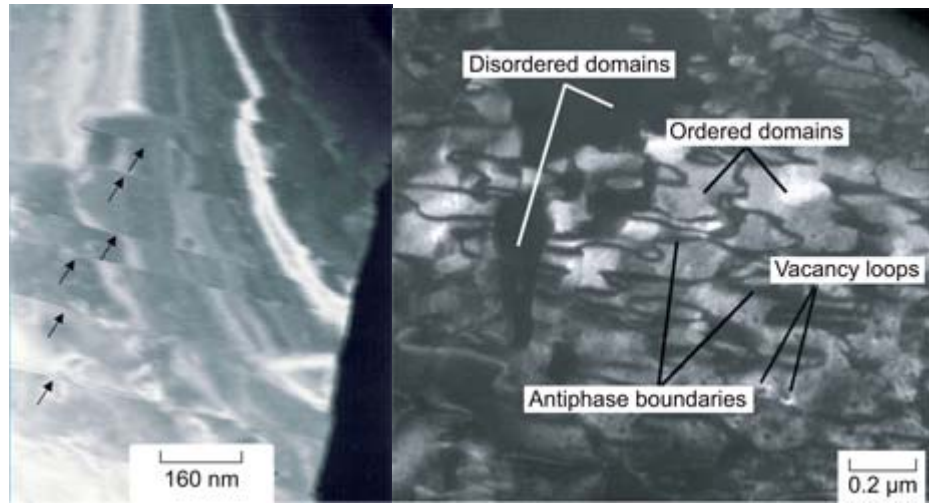
The backscattered-electron scanning electron micrograph image shown here, along with the superimposed schematic drawing, illustrates a compositional segregation (core-shell) produced by the melt process for  $\text{Sr}_3(\text{Ca}_{1+x}\text{Nb}_{2-x})\text{O}_{9-\delta}$ . The core of the cells is richer in calcium and strontium, whereas the shell of the cells is richer in oxygen and niobium, as revealed by the wavelength-dispersive x-ray chemical mappings shown in the following graphs. Determined by impedance spectroscopy, the shell regions act as resistive barriers for protonic conduction, whereas the core region exhibits higher protonic conduction for  $\text{Sr}_3(\text{Ca}_{1+x}\text{Nb}_{2-x})\text{O}_{9-\delta}$ .



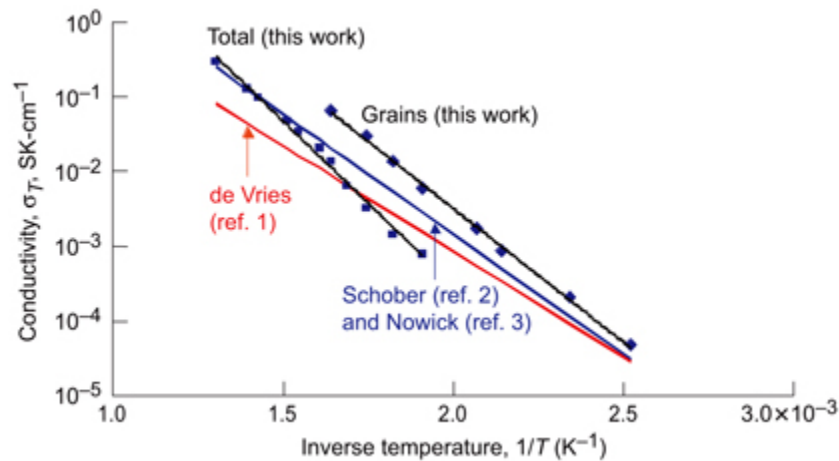
*Chemical concentration profiles across several cells (vertical lines indicate cell boundaries) of a  $\text{Sr}_3(\text{Ca}_{1+x}\text{Nb}_{2-x})\text{O}_{9-\delta}$  sample. Oxygen-rich boundaries are revealed.*

Transmission electron microscopy (TEM) examination of melt-processed HTPC materials revealed fabricated nanoscale architectures that cannot be achieved by solid-state sintering. The next two figures show dark-field images of nanoscale architectures in  $\text{SrCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$  (left) and  $\text{Sr}_3(\text{Ca}_{1+x}\text{Nb}_{2-x})\text{O}_{9-\delta}$  (right). Selected area diffraction and high-resolution TEM analysis reveal that the domains in  $\text{SrCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$  consist of a phase where the oxygen octahedras are tilted. This tilting is believed to reduce the rotation angle for the diffusing  $\text{H}^+$  ion, enhancing the transfer rate from one oxygen octahedron to

the next octahedron. This interpretation has been supported by the superior conductivity data shown in the final graph. The impedance analysis shows that the intragrain has superior conductance that can be associated with nanodomain formation. Engineering the microstructure, down to the nanoscale (as shown in the dark-field image on the left) is continuing, and our current research is focused on assembling these nanodomains on a macroscale to enhance the  $H_2$  permeability rate. The conductivity data shown in the final graph has a strong merit for hydrogen-generation technology in the temperature region of 400 to 600 °C. Applications could be in hydrogen production and separation, using small reformers and electrolyzers, or in a high-temperature hydrogen sensor for aerospace applications.



*Left: Nanodomain formation in melt-processed  $SrCe_{1-x}Y_xO_{3-\delta}$ . Boundaries indicate the oxygen cage tilting mode; arrows show the domain boundaries. Right: TEM image of  $Sr_3(Ca_{1+x}Nb_{2-x})O_{9-\delta}$  showing a complex nanodomain structure. Nanodomains exist as ordered and disordered regions. Ordered domains are separated by antiphase boundaries.*



*Grain conductivity and total conductivity of melt-processed  $SrCe_{1-x}Y_xO_{3-\delta}$  in comparison to literature values. Impedance spectroscopy measurements show a high intragrain conductance. Poor conduction of the grain boundary reduces the total conductance.*  
Long description of figure 5. Graph of conductivity in siemens-kelvin-centimeters-1 versus inverse

temperature in Kelvin-1 for total (this work), grains (this work), de Vries (ref. 1), and Schober (ref. 2) and Nowick (ref. 3).

## References

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**Case Western Reserve University contact:** Dr. Ali Sayir, 216-433-6254,  
Ali.Sayir@grc.nasa.gov

**Glenn contact:** Dr. Frederick W. Dynys, 216-433-2404, Frederick.W.Dynys@nasa.gov

**Authors:** Dr. Ali Sayir, Dr. Frederick W. Dynys, and Dr. M.H. Berger

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